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Olivier Rozenbaum, Séverinne Anne, Jean-Louis Rouet. Modification and modeling of water ingress in limestone after application of a biocalcification treatment. *Construction and Building Materials*, 2014, 70, pp.97-103. 10.1016/j.conbuildmat.2014.07.038 . insu-01057367

**HAL Id: insu-01057367**

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Submitted on 3 Sep 2014

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# Modification and modeling of water ingress in limestone after application of a biocalcification treatment

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## Highlights

Untreated and bio-treated samples of building limestone were subjected to water imbibition tests.

Changes to the water transfer properties of the stone, attributable to the bio-treatment, were measured and quantified.

A model for water transfer under these conditions is proposed, differing from the standard Washburn law.

Bio-treatment has a limited service life over the period of the experimental run.

## Abstract

Water transfers have been recognized as the main vectors of alteration and are responsible for pore network modifications in building stone. Among the techniques used to limit or stop the penetration of water into the stone, the calcification properties of bacteria have been investigated and used to treat buildings. In this article we study the effect of such a treatment following a protocol used *in situ*. The effects of this biotreatment on limestone (here tuffeau) were measured over a large number of drying–imbibition cycles. As the imbibition curves did not follow the usual Washburn law, a model based on a space-dependent permeability coefficient is proposed. It leads to a non-linear diffusion model which accounts for the deviation from the standard Washburn model.

## Keywords

- Historical limestone;
- Biomineralization;
- Water transfer;
- Imbibition;
- Non-linear diffusion

## 1. Introduction

The causes of building stone decay are both numerous and varied, covering physical, chemical and biological actions [1], [2] and [3]. Among the most devastating causes, air pollution, salts and biodeterioration are the most frequently cited in the recent literature (e.g. [1] and references therein). The feature common to these three mechanisms is the presence of water and/or the causal role of water transfers (liquid and gas phases). The action of water within the stones is notably exacerbated by the “time of wetness” and the “time of deep wetness” as noted recently by McCabe et al. [4] due to more prolonged periods of winter wetness associated with climate changes. As water is involved in many types of stone decay [1], different surface treatments aimed at avoiding or limiting these fluxes of liquid water [5] and [6] have been developed. The most widely used are water repellents that form a film at the surface of the stone and hence exert a protective action ([1] and references therein). They give rather good results for low porosity stone as liquid water ingress is strongly limited and water impacting the stone surface drips down without causing damage [7]. However, for high porosity stones, the water repellents penetrate the pores, completely filling them up [8]. This is a real problem because gaseous and liquid water inside the stone can no longer escape but remains trapped within the porous lattice, just behind the water-repellent film, inducing alteration by frost damage for example [6], [9] and [7]. This leads to aesthetic problems and in extreme cases poses the problem of the solidity of the monument.

It is therefore necessary to prevent the intrusion of water into the stone but it is also crucial to maintain a gaseous exchange between the stone and its environment [6]. In addition, physicochemical compatibility with the treated surface is also required. For such a goal other treatments have been proposed such as organic treatments [10]. Once the role of bacteria in carbonatogenesis had been recognized, the idea was to use this property for the bioremediation of stone surfaces in historical buildings [11], [12] and [13]. One of these bioprocesses creates a calcite biocoating, the nature of which is appropriate to the substrate itself [14]. The so-called Microbially Induced Carbonate Precipitation (MICP) has been studied by several groups with the aim of reducing the surface porosity of the stones ([15] and references therein). As a result, gaseous exchange from the inside to the outside of the stone is still possible while water transfer from the outside to the inside of the stone is reduced [16].

In order to reproduce as closely as possible the real conditions of applications on monuments, in this study the stones were sprayed by a treatment (*i.e.* in accordance with industrial requirements) and not immersed within the treatment solution [15]. Laboratory treatment by immersion is favorable to bacterial development but is unexploitable in situ by stone restorers. To our knowledge only a few studies have been conducted using spraying to treat the surface stone [14]. We selected an industrial protocol developed by the Biocalcite Concept company. The aim of this treatment is to create a calcite biocoating by the bacterium *Bacillus Cereus* [17] and [16] that partially fills the pores at the stone surface. This protocol was developed mainly to protect building limestones. The creators of this process claim that their coating “ensures the protection of limestones by restricting exchange between the interior of the rock inside and external atmosphere and, additionally, by limiting the penetration of degrading agents into the stone” [16]. This process is therefore rather unclassifiable amongst stone treatment tools: on the one hand, it is not a consolidant, neither in terms of hardness nor in terms of mechanical resistance; on the other hand, it is not a hydro-repellent either, even if the bio-coating increases the liquid water time penetration (J.F. Loubière, personal communication). Note that the choice of this bacterium is not restrictive as the nature of the bacterium does not appear to be decisive for the results; the substrate has a greater influence

[14]. Like other biotreatments, the Biocalcite Concept treatment limits (but does not completely stop) the penetration of water from the exterior, while allowing gaseous fluxes in both directions.

In a previous article we characterized and analyzed the phase mineralogy produced by this biotreatment [18]. To be able to distinguish the newly formed biolayer from the substrate, the biotreatment was sprayed in the laboratory on plaster samples. The coating produced was observed by SEM, and analyzed by microprobe X and GIXD. It was shown that the composition of the coating was calcite *i.e.* a polymorphic state of calcium carbonate. The thickness of the coating was evaluated by SEM and X-ray microprobe and was found to be close to 20  $\mu\text{m}$  on plasters and on a limestone [19]. Despite this result, the penetration depth of the treatment and the coating thickness are generally rather substrate dependent [20]. Nevertheless, all the stones used in the present article were the same as in [18] and [19] and the previously evaluated thickness remains valid.

In the present article, the objectives are to quantify the modifications in the water transfer properties due to the biotreatment and to put forward a model of water transfer on a building limestone. In situ, the hydraulic properties of building stones and/or the effects of treatments are often evaluated by the Karsten pipe method [8]. However, since the objective of this work is not only to submit the stone to wetting/drying cycles in order to test and degrade (if possible) the coating, but also to quantify hydraulic modifications of the porous media, the hydraulic measurement properties were done with the imbibition method [21]. It should be mentioned that imbibition is very aggressive for the treatment, giving a lower limit of coating resistance.

The paper is organized as follows. Section 2 describes the biotreatment and the stones on which it was applied. It presents the protocol and the method used to characterize the water properties. Section 3 discusses the experimental results and proposes a model to recover them. Finally, Section 4 presents the conclusions that can be drawn from this work.

## **2. Materials and methods**

### **2.1. Material and biotreatment**

The material support for the biotreatment used in this article is a tuffeau stone [22] that was collected in a quarry located near the village of Saint-Cyr-en-Bourg (France). In the past, this stone was used to build most houses, churches, cathedrals and chateaux along the Loire valley. It is a rather soft stone and is therefore an easily workable building material. Nowadays, it is mainly used to restore these monuments. Tuffeau stone is a yellowish-white porous limestone, mainly composed of calcite ( $0.503 \text{ g g}^{-1}$ ), silica ( $0.452 \text{ g g}^{-1}$ ) in the form of opal cristobalite–tridymite and quartz, and some secondary minerals such as clays and micas. The total porosity of the tuffeau stone studied here was 48.1%. It is a multi-scale porous medium since the equivalent pore size distribution ranged from 0.01 to 50  $\mu\text{m}$  [22]. The reader is referred to the article by Beck et al. [23] for further details about the characteristics and properties of the stone.

Imbibition measurements were performed on cylindrical samples (diameter: 30 mm) that were small enough for the gravity effect to be neglected (height: 60 mm) [24]. The cylinders were all cut parallel to the sediment bedding in order to avoid undesirable anisotropic effects. Before treatment, the samples were oven-dried during 96 h at 50 °C in order to remove all

residual water. They were then placed in a desiccator with phosphorous anhydrite in order to reach room temperature while maintaining a dry environment. The capillary coefficients were calculated using three samples (three for the treated and three for the untreated samples) in order to average the local inhomogeneities of the pore lattice.

The biotreatment used in this work involves a bacterium (*Bacillus cereus*) that is particularly well-suited for limestones [17] and [16]. This technique was patented (Calcite Bioconcept firm) and has often been used on limestones [18] since it generates a calcite coating *i.e.* a material of the same nature as the stone substrate, thus ensuring optimal compatibility. It should be mentioned that this biomineralization treatment was optimized in order to be completed within one week, which is one of the restorers' requirements.

For obvious reasons of conservation, transport and implementation on a restoration building site, the bacteria were lyophilized by the manufacturer. Fifteen hours before use on the site, the freeze-dried bacteria were re-hydrated with a nutrient solution developed by the Calcite Bioconcept firm (peptones, yeast, salts, antifungus). After this lapse of time, the culture medium was sprayed onto a statue or part of a monument (about 1 L/m<sup>2</sup>). The bacteria were fed with a nutrient solution 24, 32, 48 and 72 h after spraying. The bacterial colony increased exponentially during these three days. For this study, this protocol was strictly reproduced on the cylinders described previously in this section by spraying one face (one cross-section) only. In order to be certain that the treatment was complete, the imbibition measurements presented in this work were done 40 days after the treatment. This curing time was selected as measurements done 40, 90 and 110 days after the treatment (SEM, microprobe, GIXD and imbibitions measurements) did not show any difference. The reader is referred to [18] and references therein for more details concerning the development of the process.

SEM micrographs for untreated tuffeau (Fig. 1a and b) showed sparitic and micritic calcite and spherulites of opal. After biotreatment (Fig. 2a and b) the surface was strongly modified and far less rough. Crusts covering the raw tuffeau generated a smoother surface with numerous cracks (Fig. 2b). These cracks were probably an artefact due to the high vacuum needed in the SEM chamber [18] and [19].

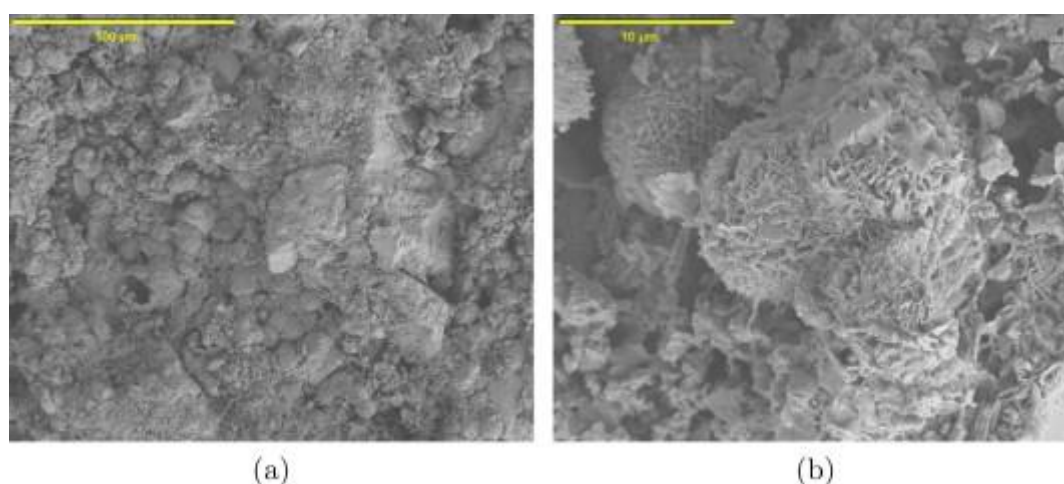


Fig. 1. : SEM image (secondary electron) of a tuffeau surface before biotreatment (a) 500×500× magnification and (b) 4000×4000× magnification.

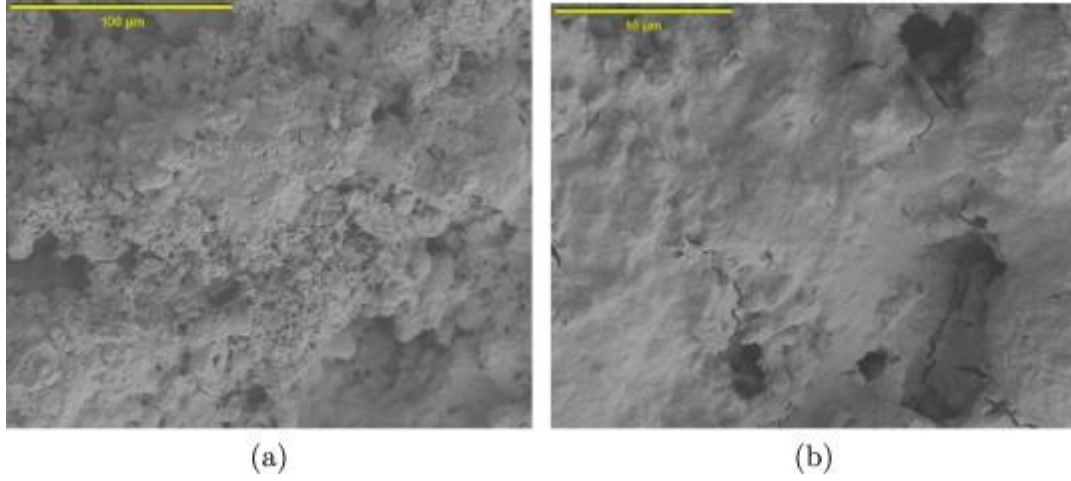


Fig. 2. : SEM image (secondary electron) of a tuffeau surface after biotreatment (a) 500×500× magnification and (b) 4000×4000× magnification.

## 2.2. Imbibition measurements

Imbibition experiments are used to describe the transfer properties of a material via the imbibition coefficients [24], [21], [25] and [26]. The lower surface of the material is placed in contact with water and due to capillary forces, the water fills the pores, pushing the air inside the pores out of the sample. The water mass uptake and the height of the capillary front can be measured as a function of time. Neglecting the gravity effect on water and assuming cylindrical pores, the Washburn law predicts an evolution that is a function of the square root of time  $t$  for both the mass uptake  $\Delta m$  per surface area unit  $S$  and the capillary fringe height  $h$  :

$$\frac{\Delta m}{S} = A\sqrt{t} \quad (1)$$

$$h = B\sqrt{t} \quad (2)$$

where the imbibition coefficients  $A$  and  $B$  are defined as follows:

$$A = \pi r^2 \sqrt{\frac{r\gamma \cos \alpha}{2\eta}} \quad (3)$$

$$B = \sqrt{\frac{r\gamma \cos \alpha}{2\eta}} \quad (4)$$

with  $r$  the radius of the capillary,  $\eta$  the water viscosity,  $\gamma$  the superficial tension and  $\alpha$  the angle between the solid and fluid. Hence, mass uptake and height of the capillary front are usually represented versus the square root of time. Thus, according to Eqs. (1) and (2), it was expected that for homogeneous stones ( $A$  and  $B$  constant) a linear increase in  $\Delta m/S$  and  $h$  with respect to  $\sqrt{t}$  [24], [21] and [25] would be recorded. In the following only the mass uptake will be presented as the capillary height gives rather redundant information.

From a practical point of view, mass uptakes were measured each minute during the first 30 min followed by larger time intervals, until stable masses were obtained. During each measure the stones were not in contact with the water tank (for about 7 s). This could lead to slight experimental errors during the first minutes as water mass uptake is important during this lapse of time.

### 3. Measurements and modeling

The effect of the treatment was assessed by comparing the imbibition curves for treated and untreated samples. Twelve imbibition–drying cycles were performed for all the samples with distilled water to determine the long term behavior of the treatment. These imbibition–drying cycles are similar to the wet–dry ageing test. After imbibition the samples were put in an oven at 50 °C until total drying. Once the mass was constant, the sample was ready for a new imbibition–drying cycle. During the drying period, the sample was wrapped in an aluminum sheet, except for the surface which was in contact with water during imbibition. To sum up, water entered or exited the sample via the same surface.

#### 3.1. Imbibition–drying cycles on untreated samples

Fig. 3 shows the time evolution of the mass uptake of water during the imbibition cycles (for cycles 1–12). In spite of the cylindrical capillary hypothesis and despite the slight experimental errors mentioned above, the imbibition curves recorded for all the untreated stone samples showed a quasi linear increase ( $\Delta m = A t \sqrt{t}$ ) within a first zone going from 0 to  $t_s$  ( $t_s$  is hereafter called the saturation time). The saturation time varied from one cycle to another, but covered approximately the [35; 45] min range. This behavior, similar to that found in [21], indicates a homogeneous porous lattice [24] and [25]. Within the following zone ( $t \sqrt{t} > 6.5 \text{ min}^{1/2}$ ), the mass uptake continued very slowly and corresponds to the infilling of the trapped porosity thanks to air diffusion through water. In the first zone (*i.e.* in the range  $[0, t_s]$ ), the slopes of the curves decreased progressively as the cycle number increased. Hence the coefficient of water absorption  $A$  decreased slightly with the number of imbibition/drying cycles. In other words, the mass uptake was longer and water saturation was reached later as the number of cycles increased. Therefore, a slight modification in the water transfer properties was observed, indicating a slight modification in the porous lattice [27].

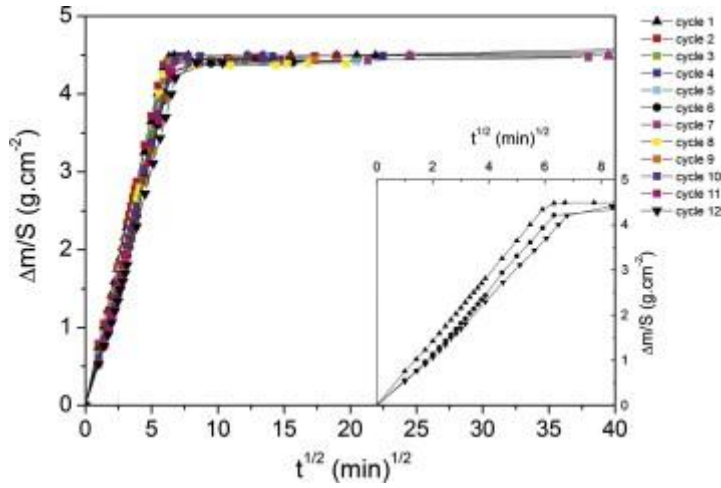


Fig. 3. : Imbibition curves for an untreated sample. The enclosed figure is an enlargement of the range  $t^{1/2} \in [0, 8]$  for cycles 1, 6 and 12. The same symbols are used in both figures.

### 3.2. Imbibition-drying cycles on treated samples

The imbibition curves (Fig. 4) for the treated samples were radically different from the untreated imbibition curves (mainly the first two cycles). Above all, the time  $t_s$  necessary to reach the saturation zone for the first cycle was considerably increased:  $t_s=680\text{min}$  (in comparison, it took approximately 40 min for the untreated cycles). But the saturation time  $t_s$  decreased for the other cycles:  $t_s=400\text{min}$  for the second cycle and  $t_s=220\text{min}$  for the third cycle. After the third cycle, the time  $t_s$  decreased slightly, reaching 140 min for the last cycle. Hence,  $t_s$  still remained higher (whatever the cycle number) than the  $t_s$  times for the untreated samples (40 min). Furthermore, while the imbibition curves increased linearly in the first zone for the untreated samples ( $\Delta m/S = At^{1/2}$ ), the imbibition curves for the treated samples presented a rather different behavior for (at least) the first two cycles. This behavior has also been observed for other treatments [10] and [28]. In view of these differences, it seems necessary to develop another model. We therefore propose a power law behavior in the following section ( $\sim t^\alpha$ ).



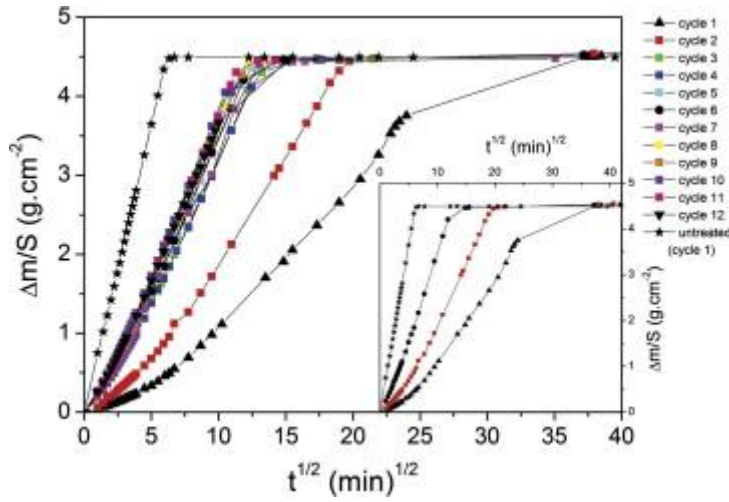


Fig. 4. : Imbibition curves for a treated sample. The imbibition curve obtained for the first cycle of an untreated sample has been plotted (stars) for comparison.

The imbibition coefficient  $A$  which is given by the slope of the imbibition curves ( Fig. 3 and Fig. 4) was computed and is plotted in Fig. 5. As expected, the values of  $A$  are smaller for the treated sample but increase with the cycle number. Nevertheless  $A$  is still lower than the coefficient obtained for untreated samples even for cycle 12. The coefficient  $A$  computed for untreated samples decreases slightly with the cycle number. So for both cases, the lattices change with the cycle number. Coefficient  $A$  was determined only if the imbibition curves nearly follow a square root of time evolution. This is not the case for the first two cycles of the treated samples, meaning that the assumptions made by the Washburn equation are no longer valid. Because the treatment modifies the surface of the samples, a non homogeneous lattice will be assumed.

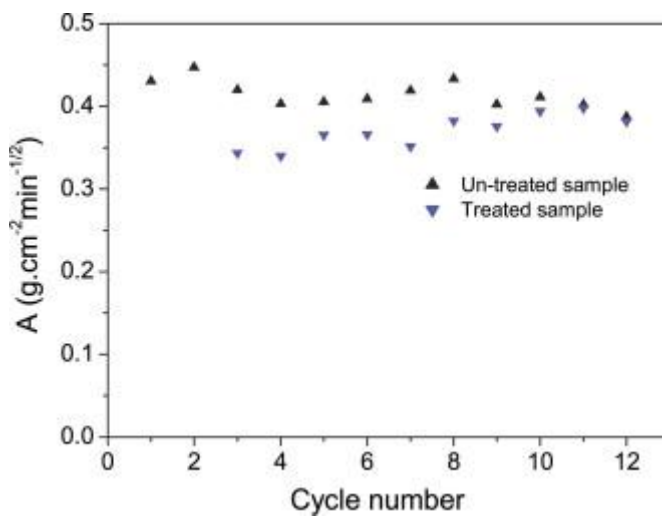


Fig. 5. : Coefficient  $A$  as a function of the cycle number for untreated and treated samples.

### 3.3. Modeling

As shown in Fig. 4 for the treated samples, while the mass uptake for the last cycles seems to be proportional to the square root of time, this is clearly not the case for the first two cycles. The log–log representation (Fig. 6) of the data of Fig. 4 shows a power law behavior. The first part (before saturation) is roughly linear and the slope gives the power index that depends on the cycle number. We therefore looked for a model which gives such an evolution. Following the work of Laurent [29] and [30], the conservative equation of the water uptake  $c(t,z)$  at time  $t$  and location  $z$  reads

$$\frac{\partial c}{\partial t} + \frac{\partial J}{\partial z} = 0 \quad (5)$$

where no border effects were considered, so a one-dimensional model was used. The  $z$  coordinate stands for the distance from the water surface. The flux  $J$  is given by Darcy's law:

$$J = -D \frac{\partial c}{\partial z} \quad (6)$$

This yields

$$\frac{\partial c}{\partial t} = + \frac{\partial}{\partial z} D \frac{\partial c}{\partial z} \quad (7)$$

which is a diffusion equation of coefficient  $D$ . As the samples are initially dried,  $c(0,z)=0$  and as the bottom of the sample is in contact with free water, the boundary condition is  $c(t,0)=1$ .  $D$  usually depends on the moisture  $c$ , but then the Boltzmann transformation gives solutions which are a function of the square root of time  $t$ . Taking into account the modification induced by the biotreatment, the dependence on  $z$  is assumed. As power-law solutions are sought after, the following equation is considered:

$$D = \frac{D_0}{z^\lambda} \quad (8)$$

With this choice, Eq. (7) is a classical model of an anomalous diffusion process [31]. The sample is assumed to be high enough for the system to be considered as semi-infinite. The solution to Eq. (7) depends only on the variable  $y$  defined by O'Shaughnessy and Procaccia [32]:

$$y = \frac{z}{t^{1/(2+\lambda)}} \quad (9)$$

If  $\lambda=0$ , the usual variable used in the Boltzmann transformation is recovered. The solution to Eq. (7), taking into account the initial condition and boundary condition reads  $c(z,t)=f(y)$ . Integrating from  $z = 0$  to infinity, the mass uptake  $\Delta m(t)$  of water by the sample during time  $t$  is obtained

$$\Delta m(t) \approx \int_0^\infty c(z,t)dz \approx t^{1/(2+\lambda)} \int_0^\infty f(y)dy \quad (10)$$

and consequently  $\Delta m(t) \sim t^\alpha$  with  $\alpha = 1/(2+\lambda)$ . If  $\lambda=0$ , the usual square root of time dependence is recovered. A linear regression was performed on the curves in Fig. 6 before the saturation time  $t_s$ . It gives the index  $\alpha$  whose evolution as a function of the cycles is given in Fig. 7. The index obtained for untreated samples was also determined and is plotted for comparison.

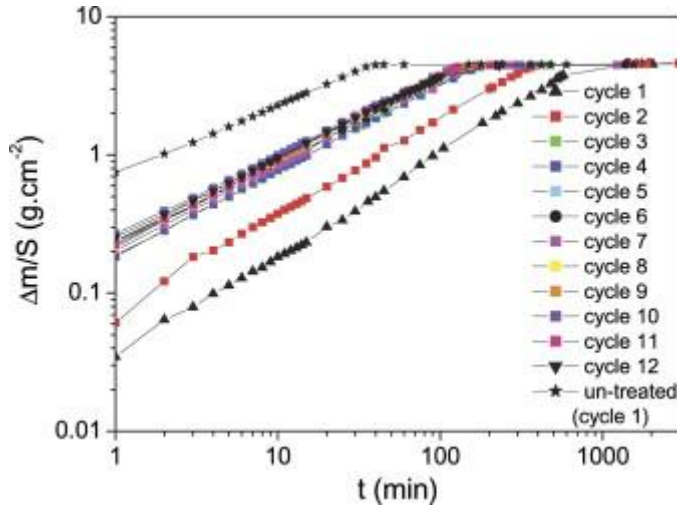


Fig. 6. : Log-log plot of the imbibition curves for a treated sample and the first cycle of a untreated sample (stars).

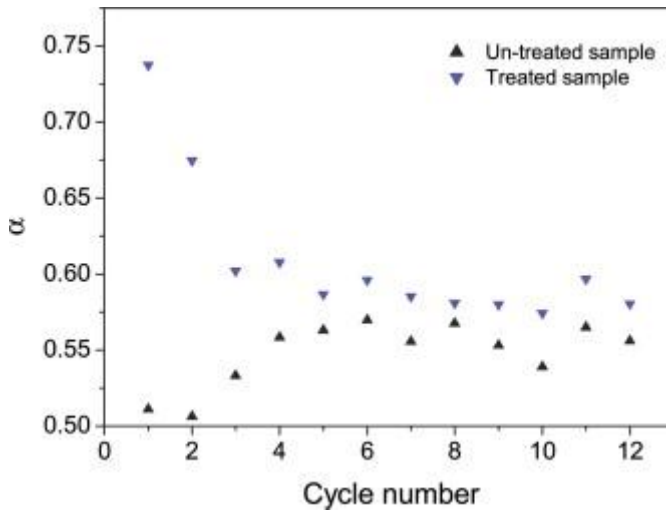


Fig. 7. : Power index  $\alpha$  as a function of the imbibition-drying cycle for biotreated and untreated samples.

For the untreated samples, the power index is around 0.5 which is the value expected for a homogeneous porous lattice [25] and [24]. However, the power index increases slightly with the cycle number. This suggests that the lattice has been modified by the imbibition-drying cycles. This was shown previously by Beck [27] who argued that dissolution and

recrystallization processes took place within the stone. The index of treated samples is around 0.7 for the first cycle. It decreases to reach a value that still remains higher than the index obtained for the untreated samples. Hence the biotreatment considerably modified the water transfer properties of the stone. But as the imbibition test is aggressive (compared to natural rain for example) the effect of the treatment is reduced after a few cycles. As previously mentioned, even for the last cycles, water transfer into the lattice of the biotreated sample is still lower than that of the untreated samples. This shows the combination of two effects: (i) the durability of a porous lattice modification induced by the biotreatment, and (ii) the lattice modification induced by the imbibition–drying cycles. With  $\alpha > 0.5$ , the index  $\lambda = (1 - 2\alpha)/\alpha$  is negative, so the diffusion coefficient increases with  $z$ . This tendency is in accordance with the observation that the biotreatment, applied on the surface samples, slows down water intrusion.

#### 4. Discussion and conclusion

The water transfer behavior of a biotreatment process applied on a building limestone was studied. Treated and untreated samples were submitted to a large number of imbibition–drying cycles. It has been shown that the treatment slows down liquid water penetration into the stone (imbibition phase) while gaseous vapor can move easily from the inside to the outside of the stone (drying phase). These destructive tests also showed that the biocoating has a limited lifetime. This has been checked in situ on Thouard church (France) since 1993 where the biotreatment needed to be renewed every ten years (J.F. Loubière, personal communication).

While this removal of the coating by natural processes is one of the requirements necessary to define the treatment reversibility [33], it should be underlined that this notion of reversibility is not totally shared by a part of the conservation community as discussed by [34], [35], [36] and [37] and it demands particular care for a conservation study.

Moreover the first imbibition tests on treated samples did not follow the classical law function (*i.e.* mass uptake proportional to the square root of time). A power law model has been proposed here which takes into account the local modification of the porous lattice. It gives power law solutions which fitted the imbibition curves of all the samples studied here. Furthermore power index evolutions were observed for the treated and untreated samples showing stone evolutions (dissolution and re-crystallization) for the untreated samples and evolution of both the stone and the coating for the treated samples. Modifications of water transfer properties are mainly due to open porosity reductions on the surface [38] and to the changes in contact angle and/or interfacial energy associated with the formation of bacterial biofilms [39].

As mentioned above, the imbibition curves presented in this paper do not fit the usual Washburn law, in contrast to those presented in the literature (*e.g.* [40]). This is due to differences in the protocols followed in the studies. Firstly, they differ by the choice of the bacteria even if this choice is not the main factor impacting the results [14]. Secondly the practical applications of the biotreatment process are not the same: in our study the treatment was sprayed onto a given surface of the stone while in De Muynck et al. [40], samples were immersed within the liquid treatment. In the latter case, one can expect to obtain an in-depth treatment with a more homogeneous biodeposition in the whole volume of the porous matrix, whereas the spray treatment is more localized to the surface of the stone as pointed out by

Anne et al. [18]. Consequently, the model developed in the present article is perfectly suitable for the spray treatment *i.e.* with a coefficient of diffusion  $D$  depending on the depth.

It should be mentioned that power law imbibition curves are also recovered when dealing with fractal porous media (see [41] and references therein). In that case, the pore space distribution is also a power law [42].

This simple and feasible approach has some drawbacks. First, the coefficient  $D(z)$  is free scale. Then, no information on the treatment depth is available. Furthermore, the first two cycles of the treated sample reveal more than one scaling range (see the two distinct zones in Fig. 4). Hence, a single index is insufficient to monitor the time evolution of the mass uptake  $m$ . This may be related to a time evolution of the biocoating itself during imbibition which is manifested as a time dependence of the coefficient  $D$ . Nevertheless the index  $\alpha$  gives highly sensitive information on the change in porous media properties. We believe that this index could be profitably used in other studies.

This preliminary study was conducted in favorable growing conditions for the bacteria development (controlled temperature and relative humidity) and future trials should be carried out in real environments. These studies will be conducted using the same protocol and the same sort of stone presented in this paper but under varying thermo-hygrometric conditions. This should enable us to observe and to characterize the development of *Bacillus Cereus* following varying conditions (or in situ conditions) on a given stone. For the moment, the only monitoring that has been carried out concerns Thouard church (built with another kind of stone) without complete characterization of the coating.

The characterization of the bio-coating effect could be completed by a set of experimental measurements such as gas permeability (preliminary results showed a permeability reduction of 35% caused by the coating), free water absorption, forced water absorption and drying measurements [43] on untreated and treated samples.

Finally, these results were obtained for a high porosity limestone and precautions should be taken for lower porosity stones. This aspect needs to be addressed in a future study.

## Acknowledgments

We thank J.-F. Loubière from Calcite BioConcept for his support and for supplying the biological material as well as for interesting discussions. This study was partially financed by the “Région Centre”, France (PASTIS project).

The authors would also like to thank three anonymous reviewers for their valuable comments and suggestions.

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